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奈米有機材料的模擬和計算
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Part 1.

Comparative Molecular Field Analysis Study of Flavonoids Active against HT-29 Colon Carcinoma

Abstract:

Flavonoids are found in various food items of plant origin. In vitro, flavonoids are known to be antiproliferative for a varieties of cancer cells. Many efforts for the development of chemopreventive or therapeutic agents for cancer from natural products have been performed over the last several decades. In this research, A series of 31 flavonoids that showed cytotoxicity against human colon carcinoma (HT-29) was analyzed using comparative molecular field analysis (CoMFA) for defining the hypothetic pharmacophore model. To perform systematic molecular modeling of these compounds, a conformational search was carriedout based on the precise dihedral angle analysis of the flavone. After determining the energy-minimized conformers of the flavone, CoMFA was performed using several different alignments. The three dimensional (3D)-quantitative structure–activity relationship study resulted in reasonable statistical value.

Keywords: Flavonoids; antiproliferative; cytotoxicity; colon carcinoma; HT-29; CoMFA

Introduction:

Comparative Molecular Field Analysis (CoMFA) has been widely used as a powerful 3D-QSAR (Quantitative Structure-Activity Relationship) tool in the field of medicinalchemistry. In CoMFA, steric and electrostatic field variables are calculated with a probe atom at intersections of three-dimensional lattice around the compound using Lennard-Jones and Coulomb potentials. Then the statistical model is constructed between their field variables and biological activities of molecules. Usually the PLS (Partial Least Squares) method is used as a regression method. The results of CoMFA can be easily understood by drawing contour plots of regression coefficients of a PLS model.

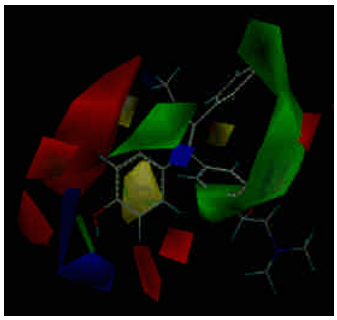


Figure. 1 CoMFA diagram

Green Steric bulk favored

Yellow Steric bulk disfavored

*Blue*Positive charge and H-bond donors favored

Negative charge and H-bond acceptors disfavored

*Red*Negative charge and H-bond acceptors favored

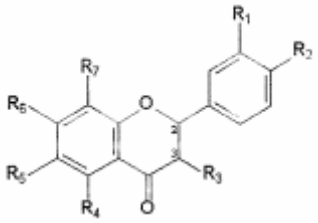
Positive charge and H-bond donors

disfavored

Discussion:

The computational calculations were performed using the molecular modeling software Sybyl 6.30 with the standard bond lengths and angles. Molecular mechanics calculations including field-fit optimization were carried out with Tripos force field and the minimum energy change of 0.05 kcal/mol as a convergence criteria. Changes were calculated using the Gasteiger-Huckel method as implemented in Sybyl.

Table.1 Antiproliferative activities of polymethoxylated flavones against human colon cancer cell line (HT-29).



compounds	HT-29 IC50 value 【μM】	pIC50
(!) 3,5,6,7,8,3',4'-heptamethoxyflavone	2.10	5.68
(2) tangeretin	1.60	5.80
(3) nobiletin	4.70	5.33
(4) sinensetin	9.50	5.02
(5) tetra-*O*-methylscutellarein	6.30	5.20
(6) 5-desmethylnobiletin	8.50	5.07
(7) tetra-O-methylisoscutellarein	6.60	5.18
(8) 5-desmethylsinensetin	5.00	5.30
(9) quercetin 3,5,7,3',4'-pentamethyl ether	33.00	4.48
(10) quercetin 3,7,3',4'-tetramethyl ether	0.84	6.08
(11) limocitrin 3,5,7,4'-tetramethyl ether	45.00	4.35
(12) quercetin 5,7,3',4'-tetramethyl ether	15.60	4.81
(13) limocitrin 3,7,4'-trimethyl ether	54.00	4.28
(14) quercetin 5,7,3',4'-tetramethyl ether-3-acetate	14.00	4.85
(15) limocitrin 3,7,4'-trimethyl ether-5-acetate	18.00	4.74
(16) quercetin 3,7,3',4'-tetramethyl ether-5-acetate	15.00	4.82
(17)	18.00	4.74

Table.2 CoMFA statistical result.

compound	Act.	Pred.	SEE
1	5.68	5.65	0.03
2	5.8	5.89	-0.09
3	5.33	5.34	-0.01
4	5.02	4.93	0.09
5	5.2	5.16	0.04
6	5.07	5.05	0.02
7	5.18	5.18	0.00
8	5.3	5.29	0.01
9	4.48	4.78	-0.30
10	6.08	5.89	0.19
11	4.35	4.14	0.21
12	4.81	4.82	-0.01
13	4.28	4.53	-0.25
14	4.85	4.85	0.00
15	4.74	4.59	0.15
16	4.82	5.05	-0.23
17	4.74	4.6	0.14

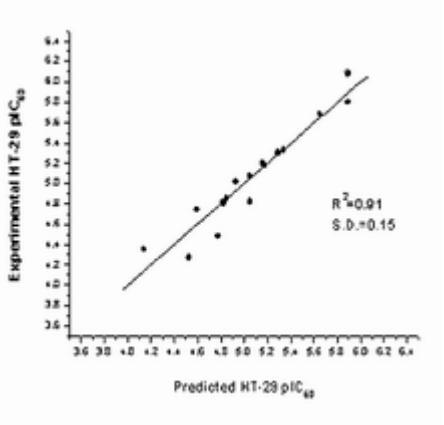


Figure.2 A correlation plot of actural activity and predicted

5,8-dihydroxy-3,7,3',4'-tetramethoxyflavone			activity values for 17 flavonoids.

Finally, we choosed 17 flavonoids to construct the3D QSAR model.(Table.1) The CoMFA statistical results for the cytotoxic activity of HT-29 are summarized in Table. 2. As a result, the plot of the calculated and observed pIC_{50} gives a good correlation coefficient R^2=0.91 as shown in Figure. 2.

Conclusion:

The results suggested that the bulky group substituent at R_2 and R_7 positions would enhance antitumor activity, and the yellow region at R_4 favored less bulky group. This assumption also agreed with the phenomenon as shown in table.1.

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Part 2.

DFT-PCM Studies of the Solvent Effects on the Absorption Properties of DCM

Abstract:

In this paper, we had studied the red emitting material, 4-(Dicyanomethylene)-2-methyl-6-[*p*- (dimethyl amino) styryl]- 4H-pyran (DCM) in different polarity solvent environments, by using the *ab initio*, density functional theory (DFT-B3lyp) with the 6-31G* basis set, to achieve the optimization structure and by using the time-dependent density functional theory to obtain the optical properties in the polarizable continuum model (PCM) modeling. As the solvent polarity increasing, the DCM molecule exhibits the red shift behavior and enhances the oscillation strength. The solvent polarity has enhanced the ability of the electron transfer from the electron donor, dimethylamine group, to the electron group, electron donor, $=C(CN)_2$. The S_0 to S_1 transition of DCM belong to the π-π^* transition. The maximum absorption peaks of different solvent environments have much better agreement with the experimental results.

Introduction

Since the first report by Tang and VanSlyke in 1987 of a low voltage driven electro- luminescent diode made of small evaporated molecules[1], this area has been the subject of a growing number of studies and publications. And the organic light-emitting diodes (OLEDs) have became the significant interest studies for the next generation flat panel displays because of their better advantages such as easy to fabrication, high brightness, low power consumption, fast response time, and wide viewing angle[2,3]. For the full color display, to design the red, green, blue materials which exhibit high color purity and efficiency are necessary conditions. There are many of green and blue emitting materials with high luminescence efficiencies and reasonable color purity have already been synthesized and been realized the light emitting mechanism in OLED region. But, until now the red emitter materials with good stationary efficiency and satisfaction color purity have not to be obtained. Usually the red light in OLED is achieved by doping a few of red fluorescent dyes into host materials to let the emission peak shift more then guest red dopant in the red region[4-9]. In this kind of the red dyes, since the 1989, Tang has synthesized the 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran (DCM, scheme 1)[3] and improved a much stronger emission peak (570-620 nm) in the orange-red light region such that the DCM molecular become the excellent red emitter material[10-11].

During the past decade, lots of DCM studies have proved that the it is the very

efficient laser dye which widely used for a t unable light source in a broad spectral region[10,11]. And the photo- physical process of the DCM molecular has also been the subject of several studies[12-20]. Many of papers have present that DCM can undergo a twist about the central ethylenic double bond to a chive the photoisomerization or about the bond connected the dimethylamino group and the phenyl ring to result in the twisted intramolecular charge transfer (TICT) state[18-23]. In addition to the TICT state, DCM contains a freely rotating electronic donating group (dimethyl- amino, -$N(CH_3)_2$ and a strong electron acceptor group ,-$C(CN)_2$ which is connected by a stilbene-like fragment. In the electronically excited state of DCM, the electron density has transferred intramolecularly such that the excited state dipole moment (26.3D) of DCM is much higher than the ground state dipole moment (5.6D)[16]. It is manifested the red shift in the both absorption and emission spectra of the DCM molecule in different polarity solvents.

In 1992, Marguet presented the nature of the TICT state and the solvent-induced trans-cis isomerization of the DCM compound by using the semi-empirical CS INDO MRCI method[24]. Through the study of the potential energy curves, dipole moment and the charge distribution with twisting different bonds in DCM molecule, their group have proved the most reasonable TICT state of DCM and the relationship between the solvent polarity and the trans-cis isomerization of DCM. Recently, the femtosecond fluorescence up-conversion technique and the TD-DFT cal-culations has already performed by Diau to investigate the nonradiative dynamic process of DCM in nonpolar solvent[25]. In 2004, our group have been reported the electroluminescent pro-perties in red emission DCM, DCJ, RED and DAD dericatives by using semiempirical AM1 with ZINDO and ab initio DFT with TD-DFT methods[26]. The result shows a good agreement with experimental result. Apart from this, however, there have yet the systemic theoretical investigation of the red shift nature of the absorption spect ra of DCM molecule.

Generally, for the reduction the time consumption, it is necessary to assume that the interesting system is in the vacuum surrounding with using the quantum mechanic calculation.

For simulation the solvent environment, we can use two kind of model: the first is the continuum model; the second is the discrete model[27]. The continuum model regards solvent as the continuum medium, and through this model, we can obtain the physical properties in the total solvent environment. The discrete model regards the solvent as a molecule, and we can investigate the solvent-solute interaction to know the detail influence by reasonable assumption the reaction site of the solvent-solute and the mount of the solvent.

In this paper, we have studied the nature of the red shift in absorption spectra of

DCM in different polarity solvents with using the polarizable continuum method (PCM) and time-dependent density functional theory (TD-DFT). The geometry parameters, the maximum absorption peak, and S_0-S_1 transition type with different polarity solvent have been considered in this paper.

Calculation methods

The ground state geometries of DCM in different solvent environment was fully optimized by the density functional theory, b3lyp and the hartree fock, HF method with 6-31G* basis set. The frequencies calculation had been achieved for obtain the reasonable structure. The spectra properties of DCM molecule such as the maximum absorption peaks, the oscillation strength were calculated with the TD-DFT method with 6-31G* level. For the approaching the real case of the different DCM solutions and reduction the time consumption, totally calculation had performed with the PCM model to discuss the solvent effect of DCM molecule.

Theoretically, the solvent-solute modeling are described in terms of a solvent reaction field which can be partitioned into many contributions of different physical origin, related to dispersion , repulsive and electrostatic forces between solvent and solute molecules[28].

The PCM model is belonging to the quantum-mechanical (QM) method. In this kind method, the solute molecule is studied *ab initio* and the interaction with the solvent are taken into account through the reaction potential, $\hat{V}_R$, which acts as a perturbation on the solute Hamiltonian :

$\hat{H}^0\Psi^0 = E^0\Psi^0$ *in vacuo*

$[\hat{H}^0 + \hat{V}_R]\Psi = E^0\Psi$ in solution

Where $\hat{H}^0$ is the Hamiltonian of the solute *in vacuo* (including nuclear repulsion terms), Ψ^0 and Ψ are the solute wavefunctions *in vacuo* and in solution, respectively. Among this QM reaction field methods, the polarizable continuum method (PCM) has spread out since its introduction in 1981 because of its adaptability and accuracy[28-30]. Within this method, the electrostatic component of the reaction potential has to be added to $\hat{H}^0$ in order to get the effective Hamiltonian, and the electrostatic component is described in terms of a set of induced point charge $\{q_i\}$ placed at the center of small elements covering the cavity in the dielectric medium, where the solute is embedded.

In this study, all of the electronic structure and spectra property calculations were performed by using Gaussion03 software package[31].

Discussion and results

The optimized structure of DCM molecule in the vacuum environment has already done by using HF and DFT (b3lyp) methods with 6-31G* basis set. The structure parameters had showed as table 1. Both of two calculation results exhibit the fact that the most stable conformation of DCM molecule is the planer conformation. The bond abbreviation from the C_3-N_1 bond, and C_2-N_1 bond to the N_1-C_4 bond has implicated the nature that the nitrogen atom of the dimethylamine group donated its long pair electrons to take part of bonding with the carbon atom of the nearing aromatic ring to extend the π-conjugation path. There are the same situation in the alternative bond length at the aromatic ring which connected to the dimethylamine group, the resonance energy has be broken down by the strong electron donor, dimethylamine group, and two pair of π electrons have been localized at the C_5-C_7 bond and C_6-C_8 bond and the third pair of the π electrons has to play a part in transfer electrons from electron donor to electron acceptor.

Because of the defect that the correlation effect term in the Hamiltonian operator with HF design, the situation of the different bond length parameters between of two calculation results in table 1 can be realized. In general, for modeling the higherπ-conjugation system such as the OLED, OFET system, it is a much reasonable result by using the DFT method.

From the experimental results had shown the nature that the maximum absorption peaks of DCM molecule exhibit red shift phenomenon from the weak polarity solvent (cyclohexane, 445 nm) to the strong polarity solvent (water, 480 nm). In order to understanding the influence of the solvent environment on the structure changes and the red shift nature of the DCM molecule, we had used the density functional theory (DFT, b3lyp) method, time-dependent density functional theory (TD-DFT) with 6-31G* basis set with the the polarizable continuum model (PCM) to simulate the above behaviors of DCM in different polarity solvents, such as cyclohexane, 1,2-dichloroehtane, dichloromethane, methanol, dimethylsulfoxide (DMSO), and water.

1.The structure influence of different polarity solvents on the DCM :

The optimization structure of the ground state DCM molecule in different polarity solvent

environments by using the DFT (b3lyp) method with 6-31G* basis set has been performed and shown as table 2. The calculation results shows that as DCM molecule in the small polarity solvent, such as the cyclohexane, the solvent has made much slight influence to the solute and the DCM structure has much similar to the gas phase structure. As the solvent polarity increasing, from the weak polarity solvent, cyclohexane, to the strong polarity solvent, water, the structure changes are quite

significant.

To analyze the structure parameters in the different solvent surrounding, for the electron donor group, it has shown the phenomenon that as the solvent polarity increasing, at the dimethylamine group the C_3-N_1/C_2-N_1 bond has elongated from 1.4540/1.4545Å(cyclohexane) to 1.4574/1.4578Å(water) and the N_1-C_4 bond has shorten from 1.3764Å to 1.3701Å, it has implicated that the solvent polarity has increased the ability of the long pair electrons of nitrogen atom taking part of bonding with the C_4 atom to lead the N1-C4 bond to exhibit the double bond property and to lead the C_3-N_1/C_2-N_1 bond to exhibit the single bond property. Solvent polarity has also influenced the C_9-C_{10}/C_{11}-C_{12} bond to be abbreviated from 1.4490/1.4394 Å(cyclohexane) to 1.4443/1.4334 Å(water) and the C_{10}-C_{11} bond to be elongated from 1.3573 Å(cyclohexane) to 1.3627 Å(water). For the electron acceptor moiety, there are the similarity situation that the solvent polarity have the capability to let the electron withdraw ability increasing, and to result in the C_{16}-C_{19} bond elongation from 1.3977 Å(cyclohexane) to 1.4133 Å(water) and the C_{19}-C_{20}/C_{19}-C_{21} bond abbreviation from 1.4220/1.4221 Å(cyclohexane) to 1.4164/1.4167 Å(water). It is perhaps a importance factor that the electron transfer effect from the dimethylamine group to the pyran ring increasing by the solvent polarity such that the structure changes have depended on the different solvent environment.

2.The charge distribution of DCM molechle with different solvent polarity

The charge distribution of the optimization structure of the ground state DCM molecule in

different polarity solvent environments by using the DFT (b3lyp) method with 6-31G* basis set has been performed and shown as table 3. The calculation results shows that as DCM molecule in the small polarity solvent, such as in the cyclohexane, there are slight different which comparing th the gas phase. As the solvent polarity increasing, the charge of the N_1 atom has been more “positive”, from 0.471 (cyclohexane) to 0.469 (water), and the charge of C_{19} atom has been more “negtive”, from 0.017 (cyclohexane) to -0.010 (water). It has implicated the evidence that the solvent polarity condition has influence the charge transfer from the electron donor, dimethylamine group, to the electron acceptor, $=C(CN)_2$.

3.The electron transfer properties of DCM molecule in different solvent conditions:

From the experimental result of the DCM, it has showed the evidence that the red shift of the DCM had depended on the solvent polarity. Therefore, in this study, we have calculated the electron transfer properties by using the time-dependent density functional theory and using the PCM model to simulate different solvent environments, and to compare the calculation results with experimental data, show as

table 4.The maximum absorption peaks,λ_{max}, of DCM molecule exhibit the red shift effect when the solvent polarity increasing. It have much agreement with the experiment data and the calculation results by using the PCM model are acceptable.

To analyze the major MO transition contribution of this absorbance peak of DCM molecule is HOMO to LUMO transition, belong to the π-π^* transition. In the gas phase, the electron contribution of HOMO orbital concentrate on the nitrogen atom of the dimethylamine group and on the aromatic ring moiety; the electron contribution of LUMO orbital concentrate on the pyran ring and on the electron donor, $=C(CN)_2$. As the solvent polarity increasing, the electron clouds of the HOMO orbital of DCM molecule exhibit the nature of focusing to the electron donating group, and the neighboring aromatic ring, and the electron clouds of LUMO orbital exhibit the nature of concentrating on the pyran ring and on the electron donor, $=C(CN)_2$. In the HOMO orbital, the orbital population of the nitrogen atom of the dimethylamino group had arisen from the 12.74% (gas phase) to the 17.21% (methanol). In the LUMO orbital, the orbital population of the C_{19} atom of the electron withdrawing group had arisen from the 6.21% (gas phase) to the 10.15% (methanol)

Conclusion

In this study, we had simulated the optimized structure and the electron transition properties in different solvent polarity environment, cyclohexane, 1,2-dichloroehtane, dichloromethane, methanol ,dimethylsulfoxide (DMSO), and water by using the density functional theory and the PCM model. Comparing the structure parameters with different polarity solvent environment can show the nature that when the solvent polarity increasing, it has exhibited the fact that the long pair electrons on the nitrogen atom of the dimethylamine group has showed the stronger electron transfer ability, and produced the bond length between the nitrogen atom of the electron donating group and the neighboring aromatic ring abbreviation. For the electron acceptor moiety, there are the similarity situation that the solvent polarity have the capability to let the electron withdraw ability increasing, and to result in the C_{16}-C_{19} bond elongation. All of this structure parameters exhibits that the electron transfer ability of the DCM molecule dependent on the solvent polarity.

The electron transition properties of DCM in different solvent environment had been calculated by using the TD-DFT method with PCM model simulation. Calculation results had showed the fact that the red shift of the absorption peak of DCM molecule dependent on the solvent polarity, and had much better agreement with the experiment data. The MO transition type of DCM belongs to the HOMO-LUMO transition. By using PCM model to simulate the different polarity solvent environment, shows the nature that increasing the solvent polarity, the electron cloud in the HOMO orbital of DCM concentrating on the electron donating

group and neighboring aromatic moiety; the electron cloud in the LUMO orbital concentrating on the pyran ring and the electron withdrawing group.

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Scheme 1. The structure of DCM.

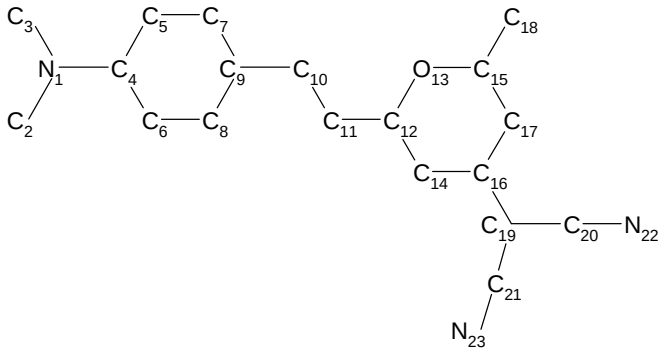

Table 1: The structure parameters of DCM molecule by using the HF and DFT(B3lyp) methods with 6-31G* basis set.

Bond distance (Å)	DCM	
	HF/6-31G*	B3lyp/6-31G*
C_3-N_1	1.4458	1.4539
C_2-N_1	1.4462	1.4544
N_1-C_4	1.3714	1.3764
C_4-C_5	1.4027	1.4167
C_4-C_6	1.4083	1.4203
C_5-C_7	1.3790	1.3852
C_6-C_8	1.3742	1.3827
C_7-C_9	1.3922	1.4093
C_8-C_9	1.3968	1.4113
C_9-C_{10}	1.4630	1.4494
C_{10}-C_{11}	1.3334	1.3573
C_{11}-C_{12}	1.4547	1.4394
C_{12}-O_{13}	1.3451	1.3713
C_{12}-C_{14}	1.3436	1.3683
O_{13}-$C1_5$	1.3446	1.3653
C_{14}-C_{15}	1.4383	1.4291
C_{15}-C_{17}	1.3322	1.3515
C_{16}-C_{17}	1.4480	1.4431
C_{15}-C_{18}	1.4933	1.4934
C_{16}-C_{19}	1.3683	1.3973
C_{19}-C_{20}	1.4315	1.4225
C_{19}-C_{21}	1.4316	1.4227
C_{20}-N_{22}	1.1384	1.1666
C_{21}-N_{23}	1.1384	1.1665

Table 2: The optimization structure of DCM molecule by using the DFT(B3lyp) methods with

6-31G* basis set and the PCM model in different polarity solvent environment.

Bond length (Å)	DCM						
	gas phase	c-hexane	CH_2ClCH_2Cl	CH_2Cl_2	Methanol	DMSO	Water
C_3-N_1	1.4539	1.4540	1.4570	1.4569	1.4573	1.4575	1.4574
C_2-N_1	1.4544	1.4545	1.4573	1.4573	1.4576	1.4578	1.4578
N_1-C_4	1.3764	1.3762	1.3706	1.3707	1.3702	1.3701	1.3701
C_4-C_5	1.4167	1.4169	1.4203	1.4202	1.4207	1.4208	1.4209
C_4-C_6	1.4203	1.4205	1.4239	1.4238	1.4244	1.4244	1.4245
C_5-C_7	1.3852	1.3850	1.3840	1.3841	1.3840	1.3839	1.3841
C_6-C_8	1.3827	1.3826	1.3817	1.3817	1.3817	1.3817	1.3818
C_7-C_9	1.4093	1.4096	1.4125	1.4123	1.4128	1.4129	1.4130
C_8-C_9	1.4113	1.4119	1.4143	1.4142	1.4147	1.4148	1.4148
C_9-C_{10}	1.4494	1.4490	1.4446	1.4449	1.4445	1.4441	1.4443
C_{10}-C_{11}	1.3573	1.3576	1.3621	1.3619	1.3627	1.3628	1.3627
C_{11}-C_{12}	1.4394	1.4391	1.4343	1.4345	1.4338	1.4336	1.4334
C_{12}-O_{13}	1.3713	1.3711	1.3667	1.3668	1.3661	1.3660	1.3661
C_{12}-C_{14}	1.3683	1.3690	1.3758	1.3755	1.3769	1.3769	1.3772
O_{13}-C_{15}	1.3653	1.3652	1.3605	1.3607	1.3600	1.3598	1.3600
C_{14}-C_{16}	1.4291	1.4288	1.4203	1.4205	1.4190	1.4190	1.4184
C_{15}-C_{17}	1.3515	1.3519	1.3552	1.3551	1.3557	1.3558	1.3557
C_{16}-C_{17}	1.4431	1.4427	1.4390	1.4391	1.4383	1.4384	1.4378
C_{15}-C_{18}	1.4934	1.4931	1.4919	1.4920	1.4918	1.4917	1.4918
C_{16}-C_{19}	1.3973	1.3977	1.4106	1.4103	1.4128	1.4128	1.4133
C_{19}-C_{20}	1.4225	1.4220	1.4173	1.4174	1.4165	1.4164	1.4164
C_{19}-C_{21}	1.4227	1.4221	1.4178	1.4179	1.4170	1.4170	1.4167
C_{20}-N_{22}	1.1666	1.1669	1.1684	1.1684	1.1688	1.1688	1.1689
C_{21}-N_{23}	1.1665	1.1668	1.1683	1.1682	1.1686	1.1686	1.1688

Table 3. the maximum absorption wavelength λ_{max}^{abs} and the oscillation strength of DCM in different solvent by using TD-DFT method and PCM modeling.

Solvent	Calculated λ_{max}^{abs} (nm) with PCM	Experimental λ_{max}^{abs} (nm)[a]
c-hexane	466.92(1.2123)*	445
CH_2Cl_2	484.77(1.2482)*	460
CH_2ClCH_2Cl	485.00(1.2493)*	467
Methanol	485.01(1.2525)*	470
DMSO	491.86(1.3038)*	480
Water	496.15(1.2539)*	480

國外差旅心得報告

王伯昌

第十二屆量子化學會議於本年度5月15號至5月19日於日本京都舉行，由京都大學主辦。本次會議中，我發表了兩篇論文：

1. A DFT-PBC Study of Infinite Single-Walled Carbon Nanotubes With Various Tubular Diameters
2. A Kinetic Monte Carlo Study of The Various Terrace Width and Step Barrier in Thin Film Growth

國際量子化學會議為每三年舉辦之大型量子化學研討會，此會議有近兩千人參加當然也包括日本本地的研究生以及學者。台灣參加人數也大約為三十位左右，其中包括中研院李遠哲院長也是受邀請獎席之一。此次大會在京都之大型會議中心召開，設備相當好，其安排的議程也相當周到。這次的會議議程安排可為我們未來召開的研討會之借鏡。